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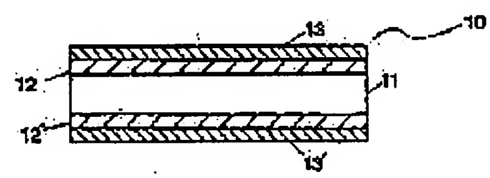
(54) COMPOSITE HYDROGEN SEPARATION METAL MEMBRANE

(57)Abstract:

PURPOSE: To obtain a stable composite metal membrane having hydrogen permeability and hydrogen selectivity for separating hydrogen from other gases.

CONSTITUTION: This composite metal membrane 10 is provided with a hydrogen permeable non-porous base metallic layer 11 and hydrogen permeable non-porous coated metallic layers 13 and 13', which are separated from the non-porous base metallic layer 11 with hydrogen permeable intermediate layers 12 and 12' and each of the intermediate layer is not a pure metal or a metal alloy and is one free from forming a thermodynamically hydrogen non-permeable layer at 400-1,000°C by the reaction with hydrogen, the base metal or the coated metal.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the approach of separating hydrogen from other gases using the compound metal membrane for hydrogen separation, and this film.
[0002]
[Description of the Prior Art] The hydrogen permeable film is better known than before, and it is usually classified into three kinds of a poly membrane, the inorganic (nonmetal porosity or nonporosity) film, and precise metal membrane (nonporosity). A poly membrane has a limitation in the selectivity over hydrogen as compared with other gas, and it has the fault that a limitation is in the resistance over the reactant chemical which has existed in the resistance over an elevated temperature, and typical distributed gas further.
[0003] For example, the hydrogen permeable film of the porosity which consists of an aluminum oxide, silicon oxide, titanium oxide, a magnesium oxide, chrome oxide, tin oxide, and an inorganic molecule like various zeolites is studied. As an example, there are some which are indicated by "Hsief, 33 Catal.Rev.Sci.Eng.1 (1991)." Although this film shows very high hydrogen permeability, these have the fault of presenting hydrogen selectivity very low for the property of porosity. It is also known that a nonporous inorganic oxide has permeability to the hydrogen of an ion gestalt. U.S. Pat. No. 5,094,927 -- the [of silicon oxide and a periodic table] -- the [the oxide of an IVB group, VB group, a VIB group, and a VIII group, and / of a periodic table] -- an IIA group and ** An IIIB group's fluoride is used as the base and the ingredient (a solid-state proton conductor is called) which has permeability to a hydrogen ion is indicated. Furthermore, the diffusion coefficient to which a hydrogen ion penetrates the oxide of molybdenum and a tungsten is reported by "JCS Faraday Trans.I.730" (1976) of Sermon and others.
[0004] This solid-state proton conductor is used by installing these between the cathode in a fuel cell, and an anode, and, thereby, transportation of the net of hydrogen is performed between a cathode and an anode. However, this solid-state proton conductor is usually weak, and permeability over hydrogen is comparatively low, and, generally he does not have a report about the use as a hydrogen demarcation membrane. As an exception, there is nonporous silicon oxide film and it is reported for this film to be able to make hydrogen penetrate through silicon oxide according to the activation surface-transport mechanism along a grain boundary. Gavalas ** -- refer to "44 Chem.Eng.Sci.1829" (1989). Although this precise silicon oxide film has very high selectivity [as opposed to hydrogen as compared with nitrogen], its reactivity with the steam in an elevated temperature is too weak and high, and the application is restricted further.
[0005] The precise metal membrane (nonporosity) which has alternative permeability to hydrogen is also well-known. the [both whose United States patents are / for example, / like / are indicated by United States patent 4,388,479th and No. 3,393,098, and / for example, the palladium alloy catalyst film] -- the [a VIIB group and] -- a VIII group's alloy film is indicated. This metal membrane has nearly perfect selectivity to hydrogen as compared with other gases, can operate it at an elevated temperature (to about 1000 degrees C), is the point of having chemical resistance to the gas in a feed-materials style, and is superior to a poly membrane and the inorganic (nonmetal) film. However, since palladium is very expensive, efforts that a hydrogen permeability compound metal membrane will be manufactured are performed by covering some base metals of a cheap transition-metals alloy with palladium or a palladium alloy. For example, refer to U.S. Pat. No. 4,468,235 and No. 3,350,846. The palladium of a little chisel is comparatively used for the palladium or the palladium alloy which covers

this base metal top, chemical resistance is given to a base metal by this, and, in a certain case, the rate of adsorption of the hydrogen to a metal membrane front-face top increases. However, this covering metal membrane has the inclination which a covering metal diffuses in a base metal under a hot service condition, and has the fault of the proper that the hydrogen permeability and chemical resistance which are acquired by this compound metal membrane by this will disappear. The nonporous hydrogen permeability compound metal membrane is indicated by U.S. Pat. No. 4,496,373, and there is a problem of the diffusion between metals about the base metal alloy of the specific presentation covered with the palladium alloy of a specific presentation in it at this compound metal membrane. However, it is convenient, although the presentation of a palladium alloy plate and a base metal alloy is limited to the narrow range and palladium is distributed not into a base metal alloy but into a covering metal. Therefore, in case this research chooses the metal used for it not being general current, needing the severe control about an alloy presentation, and manufacturing the film, fluctuation is hardly allowed.
[0006] In order to make easy diffusion association of the hydrogen permeability metal membrane to a metal substrate, preparing an intermediate reaction layer is known. For example, the method of manufacturing the film component used for the hydrogen eliminator based on diffusion by diffusing - welding the film of palladium or a palladium alloy to the metal substrate which is not limited to the Russia country patent No. 1,058,587 is indicated. Especially for the above-mentioned Russia country patent No. 1,058,587 Saturate a hydrogen permeability covering metal with an elevated temperature first, and, subsequently the so-called hydrogen load (so-hydrogen-loaded) covering metal is cooled. It migrates to the whole area between the base metals and covering metals a base metal and whose covering metal are the areas which should be welded to ** at one after that. Make detailed powder put as "a reactant gasket", high pressure (2000-2500psi) and an elevated temperature (650-700 degrees C) are made overly to act on the complex of a metallic oxide subsequently generated, and "diffusion welding" is attained between a covering metal and a base support metal. Diffusion welding is the result of a metallic-oxide "reactant gasket" interlayer being completely returned to a pure metal by the hydrogen by which desorption was carried out from the hydrogen load covering metal. However, (1) Whether the film of palladium or a palladium alloy has adhered only to the edge section of a metal substrate through diffusion joint welding, and (2) The point whether the film of palladium or a palladium alloy has covered completely the front face of a metal substrate and diffusion joint welding is unknown. In the case of the 1st, a membranous weld zone does not need hydrogen permeability. It is only required for this that hydrogen should penetrate the non-weld of the film of palladium or a palladium alloy, the hydrogen permeability part of the film of a parenthesis is not a compound metal membrane, but it is because it is only the film of palladium or a palladium alloy rather. It is becoming so expensive that it being necessary to make the fault in this case into sufficient thickness to make the film of palladium or a palladium alloy into independence nature, therefore the film not being received. In the case of the 2nd, the bipolar membrane obtained has the interlayer of a metal or a metal alloy, and this film follows the fall of the total hydrogen permeability of the film concerned on it.
[0007] The purpose of this invention is to offer the approach of solving the above and other faults of the conventional hydrogen permeability compound metal membrane, and separating hydrogen from other gases using the outstanding compound metal membrane for hydrogen separation, and this film.
[0008] This invention relates to the approach of dividing hydrogen into other gas and selection targets, using a hydrogen permeability and compound metal membrane stable at hydrogen selectivity, and this film. The essential structure of the above-mentioned film consists of a nonporous hydrogen permeability base metal and the nonporous hydrogen permeability covering metal separated by the hydrogen permeability interlayer, however it is a pure metal or not a metal alloy but standard operating temperature, and it is thermodynamically stable in the semantics which does not react with hydrogen under existence of hydrogen, or reacts with a base metal or a covering metal, and does not form a hydrogen impermeable layer. [of the interlayer] Such bipolar membrane prevents most mutual metal diffusion between a base layer and a covering metal by the operating condition, a base metal makes it possible to hold the hydrogen permeability, and a high flow rate and a membranous long life are acquired with two properties.
[0009] All bipolar membrane and the configuration layer of those can penetrate hydrogen gas alternatively. Like before The feed gas by which the main description contains hydrogen and other gas, for example, nitrogen, a carbon monoxide, a hydrogen sulfide, a steam, ammonia or methane, ethane, a propane, or a hydrocarbon like an olefin is set to a membranous transparency side. It can use for separating hydrogen with other gas with the conventional method which consists of collecting the hydrogen which was generally 400 degrees C or more in temperature, and is related with a hydrogen

partial pressure, was contacted with the high hydrogen partial pressure by the side of membranous feed, was made to penetrate hydrogen alternatively through bipolar membrane, and was penetrated. Since the film penetrates hydrogen alternatively at <400 degree C temperature (0 degree C - 50 degrees C), for example, ambient temperature, it is used for the film separating hydrogen also at low temperature, such as this, and since membranous hydrogen permeability falls at low temperature, only an economical limit is received. Moreover, it is not necessary to collect transparency hydrogen, and it can be burned, and can be used as water or can be removed from a membranous transparency side using eradication gas. Moreover, bipolar membrane is useful also to a hydrogen separation method which is indicated by U.S. Pat. No. 5217506. The hydrogen selectivity of bipolar membrane is remarkable, and it is 500 degrees C, and is a transparency side, and the flow rate (flux) of >=0.001m3 / m2, and hr shows the selectivity of >=100 with the partial pressure of the hydrogen in ambient pressure at 100psig(s) (7.03kg/cm2 gage).

[0010] The bipolar membrane of this invention is especially stable under hot conditions. When being exposed to a transparency side with >=500 degree C and an ambient temperature at the hydrogen feeder current of 100psig(s) (7.03kg/cm2 gage), it covers at 700 degrees C for 100 hours, and especially bipolar membrane covers the consecutive operation time amount by 1500 hours at 500 degrees C, and holds >=20% of the first flow rate. As shown here, this stability can be directly returned to existence of an interlayer. the base metal of the metal membrane of this invention -- the [periodic table] -- it is chosen out of the hydrogen permeability alloy which contains hydrogen permeability transition-metals; hydrogen permeability lanthanide metal [of IB, IIIB, IVB, VB, VIIB, and a VIIIB group];, and the above-mentioned metal >= 20% of the weight, and can consider as the thickness of 10-250 microns.

[0011] Covering metals are stable hydrogen permeability transition metals chemically and physically at the temperature of at least 400 degrees C, and are **********. Preferably [choosing out of the transition metals of VIIB and a VIIIB group], and most preferably, it is the hydrogen permeability alloy which contains Fe, Mn, nickel, Pd, Pt, Ru, and the above-mentioned metal >= 20% of the weight, and it is desirable that it is the thickness of 0.01-25 microns.

[0012] Since hydrogen must be easily diffuse through each class of the film including an interlayer, an interlayer's important description be form from the matter which do not form the matter stable on a thermodynamics target, the compound, or mixture of hydrogen impermeability by react with either a base metal or a covering metal at the temperature of the range of about 400 degrees C - about 1000 degrees C. The "thermodynamically stable" matter, a compound, or mixture means the matter, the compound, or mixture which is smallness in about 10kcal/mol here in the temperature the free energy of formation, such as it, generally starts. "Hydrogen impermeability" means the matter, the compound, or mixture to which the hydrogen of a compound metal membrane or the permeability of a hydrogen ion is made to fall remarkably to hydrogen before forming hydrogen opaque medium, a compound, or mixture, or hydrogen ion permeability here, after being formed in a compound metal membrane. Here, although the hydrogen or the hydrogen ion permeability of bipolar membrane are the hydrogen pressure force of 100psig(s) (7.03kg/cm2 gage), and about 400 degrees C or more as the rate of hydrogen permeation carries out "falling remarkably", it means there being more first values after about 100-hour actuation than 80%, and falling at temperature lower than about 1000 degrees C. Especially the middle class is based on hydrogen under an operating condition (temperature of the range of 400-1000 degrees C), or is thermodynamically stable to reduction of the oxide by either of the base metals or a sulfide.

[0013] In case the matter suitable for using as an interlayer is selected, it is important to take into consideration the susceptibility of the base metal for forming an interlayer and a hydrogen impermeable layer. For example, ** of the periodic table The hydrogen permeability transition metals from IIIB, IVB, and VB group are ** of the periodic table. Reactivity is size more remarkably than the hydrogen permeability transition metals of VIIB and a VIII group. Therefore, when selecting a base metal from the former group, as for a typical interlayer, it is desirable that it is the oxide of aluminum and silicon. However, it is ** about a base metal. In selecting from VIIB and a VIII group The typical middle class A lanthanide metal, a scandium, an yttrium, aluminum, All the oxide of silicon, boron, molybdenum, a tungsten, vanadium, a hafnium, and niobium, the carbide of sulfide; silicon, and a nitride; Titanium, The carbide of niobium, vanadium, a tantalum, a hafnium, and a zirconium, a nitride, silicide; SUKAUJIUMU, and the fluoride; zeolite of an yttrium; it is desirable to select from the wide range class containing graphite; and a diamond.

[0014] The middle class is good to consider as the thickness of 0.1-300 microns, it applies him as a continuation layer between a covering metal and a base metal, and he is useful to decreasing remarkably in it not only preventing contact between a base metal and a covering metal, but all elements other than hydrogen carrying out counter diffusion between a base metal and a covering metal. An interlayer can

be taken as nonporosity or porosity, when satisfying conditions besides the above. When an interlayer is porosity, an average aperture is equal to the thickness of a covering metal layer, or what is smaller than thickness is desirable.

[0015] The suitable example of the five-layer compound metal membrane 10 equipped with the two-layer covering metal layer 13 and 13' is shown in drawing 1 at the base metal layer 11, the two-layer microporosity interlayer 12, and 12' list. an interlayer and a covering metal layer -- respectively -- two-layer -- although 13 and 13' shows to 12 and 12' list, the compound metal membrane of the essential three-tiered structure of this invention equipped with each monolayer 12 and 13 is also a useful example. Moreover, the covering metal layer 13 and 13' can also consist of 2 or a three or more-layer layer.

[0016] Manufacture of the compound metal membrane of this invention (1) The laminated layers method using high temperature and a high pressure, for example, equilibrium heat pressurization,; (2) roll clad; (3) heat evaporation; (4) chemistry - or plasma-vacuum evaporationo; it reaches. It can attain by various approaches including (5) anodic oxidation, other chemical oxidation styles, or an electrolytic oxidation method. Drawing 2 shows manufacture by temperature / pressure laminated layers method in a graph. The compound metal membrane shown in drawing 1 in front of a laminating is decomposed into drawing 2 , a sectional view shows, and the same number shows the same component among drawing. 15' It reaches stainless steel press plate 15, and is shown in drawing 2 R> 2 at the graphite gasket 14 and 14' list. The graphite gasket 14 and 14' close that a laminating media is put to air, and protect it to oxidation. As for the middle class, it is desirable by depositing an inorganic oxide or a sulfide layer on a base metal first to cover a base metal chemically. In the case of oxide, a base metal is the precursor 4 (or the amount of catalysts and Si4 (OMe) of a dark hydrochloric acid) to oxide, for example, SiCl, and WCl6. Or MoCl5 Or the solution of the alkoxide of aluminum, La, or Y is covered with spraying, spinning, or immersion, subsequently it hydrolyzes, and an oxide layer is formed. Or it is aluminum 2O3 again. A layer can form anodic oxidation or aluminum by oxidizing chemically or in electrolysis. the case of metallic sulfide -- a base metal -- a pressure and temperature only high in sulfide gas, for example, a hydrogen sulfide, -- a short time -- for example, what is necessary is to just be exposed for 5 - 15 minutes Or they are the precursor 6 to a sulfide, for example, WCl, and MoCl5 about a base metal again. Or VCl3 What is necessary is to cover a solution with spraying, spinning, or immersion, to make it react with a hydrogen sulfide by it subsequently, and just to form a sulfide layer. In addition, other approaches of putting oxide or a sulfide layer are approaches by the plasma deposition or vacuum evaporationo to a base metal of desired oxide or a sulfide.

[0017]

[Example] Hereafter, an example explains this invention.

It has an example 1 vanadium base metal layer, and they are the both sides SiO2 Five-layer nickel/SiO2 / V/SiO2 / nickel compound metal membrane which covers with a layer and comes to cover both SiO(s) two-layer with a nickel layer further were manufactured using the following procedures. The good mechanical property was given to bipolar membrane, using the vanadium disk whose diameter is 5cm and whose thickness is 152micro as a base metal layer. Chemical inertness was given to bipolar membrane, using the nickel foil whose thickness is 25micro as covering material.

[0018] It is in charge of manufacturing a compound metal membrane, and is SiCl4. By immersing a vanadium disk in 1M solution which dissolved in the methylene chloride at a room temperature, it is SiO2. The dipcoat of the thin layer was carried out to the both sides of a vanadium disk. It is SiCl4 as a methylene chloride solvent evaporates. SiO2 whose thickness it hydrolyzes quickly under existence of the moisture in atmospheric air, and is about 25micro The film formed. SiO2 Good adhesion was observed between a layer and vanadium. Next, it is SiO2 as shown in drawing 2 . The laminating of the vanadium disk and nickel foil which were covered was carried out under the pressure of 20000pound (9,072kg) at 700 degrees C for 4 hours, and bipolar membrane was manufactured. Thus, the manufactured bipolar membrane was flexibility, and when it was made to curve, it did not show the signs of delaminate.

[0019] The average hydrogen flow rate which passes along bipolar membrane was measured in 700 degrees C using the hydrogen gas supply style of 99.999% of purity of 100psig (780kPa). (Transparency hydrogen was ambient pressure.) It is mediation SiO2 on the vanadium disk of the same thickness about the nickel foil of the thickness same for a comparison. The average hydrogen flow rate which passes along three layer membranes of the contrast manufactured by carrying out a direct laminating was measured under the same conditions, without using a layer. The result of the average hydrogen flow rate (m3 / m2, and time amount) about the initial flow rate after 50-hour actuation is shown in the following table 1.

[0020]
[Table 1]

膜	流量（初期）	流量（50時間後）	初期流量%
5－層	0.9	0.6	67
3－層	0.15	0.006	4

[0021] The layer (namely, layer which has the lowest hydrogen permeability) which shows the maximum resistance to hydrogen permeability about this five-layer bipolar membrane was a thin nickel coat (the marginal hydrogen flow rates which pass along the nickel film whose diameter is 5cm, and whose thickness is 25micro were 0.9m3 / m2, and time amount). Since the actual measurement of the hydrogen permeation rate which passes along bipolar membrane was not able to exceed the transmission rate which passes along the layer of each chemically different film, the nickel coat of nickel/SiO2 / V/SiO2 / nickel film restricted the whole hydrogen flow rate.
[0022] As this example shows, he is Nakama SiO2. The five-layer compound metal membrane which has a layer is Nakama SiO2. A flow rate higher than the three-layer contrast film which does not have the layer, and a long life (67% of the initial flow rate was held) are shown, and this is SiO2. An interlayer shows that it is effective for preventing too much fall of a hydrogen flow rate.
[0023] 27 layer nickel/Cu/SiO2 of examples / V/SiO2 / Cu/nickel compound metal membrane was manufactured as follows. The vanadium disk whose diameter is 5cm and whose thickness is 152micro was used as a base metal layer. Chemical inertness was given to bipolar membrane, using the two-layer nickel/Cu foil (it manufactured by carrying out the laminating of nickel foil and 25micro Cu foil which are 6micro) whose thickness is 31micro as covering material. Thin (<=25micro) SiO2 between a vanadium disk and a nickel/Cu coat It is Si (OMe)4 to the methanol containing dark HCl of the amount of catalysts, using a layer as an interlayer. This interlayer was deposited by carrying out rotation spreading of the 1M dissolved solution at a vanadium disk. SiO2 The laminating of the vanadium disk and nickel/Cu foil which were covered is carried out almost like an example 1, and it is the Cu side SiO2 It was made to face a layer.
[0024] Thus, the average hydrogen flow rate which passes along the manufactured bipolar membrane was measured by the same approach as an example 1. It is mediation SiO2 on the vanadium disk of the same thickness about the nickel/Cu foil of the thickness same for a comparison. The average hydrogen flow rate which passes along five layer membranes of the contrast manufactured by carrying out a direct laminating was measured under the same conditions, without using a layer. The result after 72-hour actuation is shown in the following table 2.
[0025]
[Table 2]

膜	流量（初期）	流量（72時間後）	初期流量%
7－層	2.4	2.4	100
5－層	0.6	0.06	10

[0026] It is SiO2 between Cu and V so that clearly. The seven-layer bipolar membrane which has an interlayer is middle SiO2. The flow rate higher than the five-layer contrast film which does not have the layer, and the stable hydrogen flow rate were shown.
[0027] 35 layer nickel of examples / sulfuration V/V / sulfuration V/nickel compound metal membrane was manufactured as follows. nickel foil whose thickness is 6micro on the other hand was used as covering material, using the vanadium disk whose diameter is 5cm and whose thickness is 152micro as a base metal. This middle class was formed in the both sides of a vanadium disk by exposing a vanadium disk to H2 S of 30psig(s) (234kPa) for 10 minutes at 700 degrees C, using a sulfuration vanadium thin layer as the middle class. Adhesion good between a sulfuration vanadium layer and a vanadium disk was observed. Next, the laminating of the vanadium disk and nickel foil which were covered with sulfuration vanadium was carried out under the pressure of 20000pound (9072kg) at 700 degrees C for 4 hours.
[0028] The average hydrogen flow rate which passes along this bipolar membrane was measured by the same approach as an example 1, and it compared with the average hydrogen flow rate which passes along three layer membranes of the contrast manufactured by carrying out the direct laminating of the

nickel foil of the same thickness, without using a mediation sulfuration vanadium layer under the same conditions on the vanadium disk of the same thickness. The result after 50-hour actuation is shown in the following table 3.
[0029]
[Table 3]

膜	流 量 (初期)	流 量 (50時間後)	初期流量 %
5 −層	0.062	0.046	74
3 −層	0.14	0.004	3

[0030] Although the five-layer bipolar membrane which has a sulfuration vanadium interlayer showed the comparatively low hydrogen flow rate first, 50 hours after, it showed the larger hydrogen flow rate of the corresponding three-layer nickel/V/nickel contrast film which does not have the interlayer than 10 times, so that clearly. (For the flow rate which passes along the five-layer bipolar membrane of this example, a sulfuration vanadium interlayer's hydrogen permeability is SiO2. Since it was lower than a layer, it was lower than the thing of an example 1)
[0031] 45 layer Pd/SiO2 of examples / V/SiO2 / Pd compound metal membrane was manufactured as follows. Palladium foil with a thickness of 25 micrometers was used as quality of a coating, using a vanadium disk with a diameter [of 5cm], and a thickness of 30 micrometers as a base metal. SiO2 The thin layer was used as an interlayer. SiO2 A layer to each 1st page of two diameter the test pieces of 5cm of Pd thin film It is HCl of the amount of catalysts on the front face of Pd first. The thin film of the included methanol is prepared. Next, it is Si (OMe)4 until each Pd front face is covered completely, before evaporating a methanol/HCl. Si4 by the reaction with; atmospheric-air moisture made to deposit by being dropped (OMe) It is thin (<=25micrometer) SiO2 by hydrolysis. The layer was obtained. SiO2 They are two test pieces of a covering Pd foil SiO2 It has arranged on both sides of the vanadium disk under a layer. Next, all assemblies have been directly arranged on a radiographic examination cel, into the radiographic examination, the gas supply pressure of 100psig(s) (780kPa) was used, the laminating was carried out at 700 degrees C, and laminated material was obtained. The average hydrogen flow rate which passes along bipolar membrane was made into the bottom of the same condition as an example 1 about 6 timing measurement, and being stabilized in 3 / m2, and hr 25.3m about 2 hours after was surveyed. This high flow rate is the result of using the palladium which has high permeability to hydrogen by using palladium as a covering metal from not nickel or nickel / copper alloy but nickel or nickel / copper alloy. The flow rate by which after actuation of 50 hours passes along the film was uniformly maintained by 3 / m2, and hr 25.3m. This shows that the film holds 100% of the original flow rate.
[0032] Because of a comparison, it is mediation SiO2 to the vanadium foil of the same thickness about the palladium foil of the same thickness in the three-layer contrast film. It manufactured by carrying out a direct laminating, without using a layer, and the average hydrogen flow rate which passes along this three-layer contrast film was measured under the same condition. The early value of 19m, even to 3 / m2, 14m3 6 hours after hr / m2, and hr, the flow rate which passes along this three-layer contrast film decreases steadily next to 0.91m3 after 50-hour actuation / m2, and hr, and is Nakama SiO2. It was shown that the film which does not use a layer holds 5% of an initial flow rate. Moreover, five-layer bipolar membrane showed the average stream flow higher than the contrast film so that clearly.
[0033]
[Table 4]

膜	流 量 (初期)	流 量 (50時間後)	初期流量 %
5 −層	25.3	25.3	100
3 −層	19	0.91	5

[0034] Example 5SiO2 In order to show permeability with a high layer, three-layer Pd/SiO2 / Pd compound metal membrane was manufactured. The base metal was omitted using palladium as a covering metal. It covered on the 1st page which has the thin layer of SiO2 so that in an example 4 for palladium foil with a diameter [of 5cm], and a thickness of 25 micrometers. Next, it is the palladium foil test piece of other same dimensions SiO2 It arranges on covering palladium and is SiO2. The layer

was made to exist between two palladium foil. Subsequently, this assembly has been arranged in the radiographic examination cel, and the on-site laminating was carried out as in an example 5. The average hydrogen flow rates which pass along the bipolar membrane measured under the same condition as an example 1 were 3 / m2, and hr 31m.

[0035] WO3 used as example 6 interlayer In order to show permeability with a high layer, three-layer Pd/WO3 / Pd compound metal membrane was manufactured. The base metal was omitted using palladium as a covering metal. Palladium foil with a diameter [of 5cm] and a thickness of 25 micrometers is used, and they are about 94% of methylene chloride, about 5% of acetonitrile, and about 1% of Si (OMe)4. WCl6 in the included mixture By applying diluted solution to the 1st page, it is WO3. The 1st page top of palladium foil was covered with the thin layer. Si4 (OMe) SiO2 In case it hydrolyzes, as a binder, it is ******** WO3. A much more homogeneous coat is generated. It hydrolyzes promptly under existence of atmospheric-air moisture, and WCl6 is WO3. The thin film was produced. Next, it is the palladium foil test piece of other same dimensions WO3 It arranges on covering palladium and is WO3. The layer was made to exist between two palladium layers. Subsequently, this assembly has been arranged in a radiographic examination cel, and the on-site laminating was carried out as in an example 4. As a result of measuring the average hydrogen flow rate which passes along this bipolar membrane under the same condition as an example 1, 3 / m2, and hr were observed 42m.

[0036] MoO3 used as example 7 interlayer In order to show permeability with a high layer, the same three-layer Pd/MoO3 / Pd compound metal membrane as examples 5 and 6 were manufactured as follows. Palladium foil with a diameter [of 5cm] and a thickness of 25 micrometers is used, and it is MoCl5 in the solvent mixture same to oneth of them as an example 6. By making a solution put, it is MoO3. The 1st page top of palladium foil was covered with the thin layer. MoCl5,It hydrolyzes promptly under existence of atmospheric-air moisture, and is MoO3. The thin film was generated. Next, it is the palladium foil test piece of other same dimensions MoO3 It arranges on covering palladium and is MoO3. The layer was made to exist between two palladium test pieces. Subsequently, this assembly has been arranged in a radiographic examination cel, and the on-site laminating was carried out as in an example 4. As a result of measuring the average hydrogen flow rate which passes along bipolar membrane under the same condition as an example 1, 3 / m2, and hr were observed 67m.

[0037] The compound metal membrane of nickel/MoO3 / Cu/MoO3 / nickel of 85 layers of examples was manufactured as follows. The copper disk with a diameter [of 5cm] and a thickness of 250 microns was used as a base metal, and, on the other hand, the nickel foil with a thickness of 25 microns was used as covering material. MoO3 The thin layer was used as an interlayer and it was made to deposit as in an example 7 on one [of a nickel foil / each] front face with a diameter of 5cm of two piece. MoO3 They are these [of the covered nickel foil] two piece MoO3 It has arranged so that a side may adjoin two fields of copper foil. Subsequently, all these assemblies have been directly arranged in a radiographic examination cel, and carried out the on-site laminating between radiographic examinations as in an example 4. The average hydrogen flow rate which penetrates this bipolar membrane under the same conditions also in an example 1 was measured by 3 / m2, and hr 0.37m. This flow rate is equal to the flow rate which passes along a copper film (the thickness of 250 microns, diameter of 5cm) by the bottom of the conditions of the same temperature and the hydrogen pressure force. As expected, the full flow which penetrates this bipolar membrane is restricted by this copper base metal layer.

[0038] The example 95 layer Pd/Y2 O3/V/Y2 O3/Pd compound metal membrane was manufactured using the following procedure. The vanadium foil with a thickness of 25 micrometers was used as a base metal, and, on the other hand, the palladium foil of the same thickness as this was used as a covering metal. It is an yttrium in the toluene which contains HCl as a hydrolysis accelerator catalyst. Isopropoxide Y [O (i-C3H6)] 3 By dropping the aquosity / methanolic solution to contain, it is Y2 O3. The thin layer was made to deposit on the both sides of this vanadium foil. This Y [O (i-C three H6)] 3 It hydrolyzed quickly in the interior of a room of 70% of relative humidity, and the thin coat generated on this vanadium. It attained by heating emission of a superfluous solvent, and the condensation to the oxide of a hydroxide by argon flowing down, and heating the so-called covering vanadium foil at 450 degrees C for 1 hour. In this way, Y2 O3 obtained The covering vanadium foil was covered with Pd and the on-site laminating was carried out over 2 hours at 700 degrees C under the argon of 100psig (780kPa).

[0039] Through the hydrogen flow rate, it measured for 13 days to this five-layer bipolar membrane. Average hydrogen flow rates are 3 / m2, and hr 16m, when it measures under the same conditions also in an example 1, and this film was maintaining 100% of that initial flow rate. These data are this Y2O3. A layer shows that the film stability superior to the five-layer Pd/NiO/V/NiO/Pd film (see the following

example of a comparison) which contains NiO again is given from the Pd/V film which does not have the interlayer.

[0040] In order to show the advantage acquired from the hydrogen permeability interlayer of example 10 porosity, the 5 layer Pd/aluminum2O3/V/aluminum2 O3/Pd compound metal membrane was manufactured as follows. The vanadium disk with a diameter [of 2.9cm] and a thickness of 30 microns was used as a base metal, and, on the other hand, palladium foil with a thickness of 25 microns was used as a covering metal. The alumina paper ("APA-3" from the Jill Karr (Zircar) products company of the U.S. New York State New York whereabouts) which has 79% of porosity was used as an interlayer. This alumina with a diameter [of 2.9cm] and a thickness of 0.03cm has been arranged on both sides of a vanadium disk. Subsequently, the alumina exposed using palladium foil with a diameter of 3.8cm was covered. This compound metal membrane was incorporated into the trial cel, and, subsequently carried out the on-site laminating at 500 degrees C using the argon gas supply pressure of 100psig(s) (780kPa).

[0041] The average hydrogen flow rate which penetrates this bipolar membrane was measured at 500 degrees C using the hydrogen gas supply style of 99.95% of purity of 100psig (780kPa). Transmitted hydrogen was ambient pressure. Early hydrogen flow rates were 3 / m2, and hr 11.2m. After making it work for 1500 hours, the hydrogen flow rate was set to 3 / m2, and hr 11.1m. This shows 99% of an initial flow rate. For the comparison, the average hydrogen flow rate which penetrates the three-layer Pd/V/Pd contrast film manufactured by carrying out a laminating directly was measured under the same conditions, without using a mediation alumina layer for the palladium foil of the same thickness as the above at the same vanadium foil of thickness. when [which is that initial value] it decreases after 140-hour operation regularly 1.7m to 3 / m2, and hr and there is no intermediate alumina layer from 3 / m2, and hr 5.3m, as for the flow rate which penetrates this contrast film, the film holds 32% of that initial flow rate -- things were shown. Moreover, there were few flow rates which penetrate this three-layer contrast film than one half of the flow rates of five-layer bipolar membrane so that clearly.

[0042] Another five-layer bipolar membrane (Pd - 5 Ru/aluminum2 O3 / V/aluminum2 O3 / Pd - 5Ru) which has the hydrogen permeability interlayer of example 11 porosity was manufactured by the almost same approach also in the example 10. However, the alumina layer was formed from the alumina filter disk ("ANODISUKU 47 (Anodisc)" from a Watt Mann scientific company of Britain and the maid stone whereabouts) which has the thickness of about 70 microns, and the hole value of standard of 0.02 microns, and, on the other hand, the Pd - 5Ru foil with a thickness of 25 microns was used as a covering metal (Pd - 5Ru is Pd alloy containing about 5% of Ru). The average hydrogen flow rate which penetrates this five-layer bipolar membrane was measured by the same approach also in the example 10. This initial hydrogen flow rate of an average was 3 / m2, and hr 9.8m. After making it work for 400 hours, the hydrogen flow rate was set to 3 / m2, and hr 9.7m, and showed 98% of the original flow rate.

[0043] The almost same five-layer bipolar membrane as example 12 example 11 was created. However, the alumina layer was a thing from the same ingredient as the film in an example 10. 600 degrees C was used and also the average hydrogen flow rate which penetrates this film was measured by the same approach in the example 10. This initial hydrogen flow rate was 3 / m2, and hr 15.5m. After making it work for about 500 hours, in addition, this hydrogen flow rate is 3 / m2, and hr 15.5m, and did not show the fall from the original flow rate.

[0044] The almost same five-layer bipolar membrane as example 13 example 11 was created. However, this alumina layer was formed from the alumina cross ("ALK-15" from the Jill Karr products company) which has 50 - 80% of porosity, the diameter of 2.9cm, and the thickness of about 0.03cm. The average hydrogen flow rate which penetrates this film was measured by the same approach also in the example 12. This initial hydrogen flow rate was 3 / m2, and hr 18.5m. After making it work for about 200 hours, the hydrogen flow rate was set to 3 / m2, and hr 17.8m, and showed 96% of the first flow rate.

[0045] The five layer Pd/NiO/V/NiO/Pd compound metal membrane of examples of a comparison was manufactured as follows. The vanadium foil with a thickness of 25 micrometers was used as a base metal, and, on the other hand, Pd foil of the same thickness as this was used as a covering metal. nickel2 (OH) It is nickel (OH)2 on the both sides of the suspension made to suspend in a basic (pH=12) water solution to vanadium. The thin layer was made to deposit. This vanadium foil / nickel2 (OH) Covering was heated in argon atmosphere at 450 degrees C, condensation of the hydroxide was carried out to the oxide, and superfluous water was separated. Each side of this covered foil was covered with this Pd foil, and the on-site laminating was carried out over 2 hours at 700 degrees C to the bottom of the argon of 100psig (780kPa).

[0046] The average hydrogen flow rate which penetrates this five-layer bipolar membrane was measured by the same approach also in the example 1. This initial hydrogen flow rate was 3 / m2, and hr 11.3m.

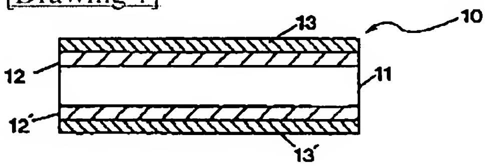
After making it work for about four days, the flow rate decreased to 3 / m2, and hr by 0.6m, and showed 5% of the initial flow rate. This result shows that the film in which a stable hydrogen flow rate is not shown is obtained by using NiO as an interlayer. It actually turns out that larger stability than the film (see the example 4) as this which does not have this middle NiO layer about the hydrogen flow rate with this same compound metal membrane is not shown.

[0047] There is no intention that the vocabulary and the expression which have been adopted on the above-mentioned specifications are not what used here for explanation and was used for limitation, and eliminate the equal object of the description indicated and illustrated by using such vocabulary and an expression or its part, and the range of this invention is specified and limited by only the claim.

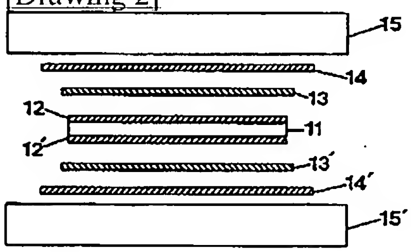
[Translation done.]

DRAWINGS

[Drawing 1]



[Drawing 2]



[Translation done.]